

# Sulfur K-edge XANES of Borosilicate Waste Glasses

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## INTRODUCTION

Many types of radioactive wastes that are destined to be incorporated in borosilicate glass for long-term safe storage (i.e. “vitrified”) contain significant amounts of sulfur. The low solubility of sulfur in silicate melts, in oxidation conditions where a waste glass melter could be safely operated, can result in sulfur becoming the waste-loading-limiting constituent [1]. Consequently, methods to improve the sulfur loading are of considerable importance and these, in turn, would benefit by understanding the structural aspects of sulfur incorporation in borosilicate glasses. To that end, X-ray absorption near edge spectroscopy (XANES) has been used to characterize the sulfur coordination environments in borosilicate glasses. XANES has the unique advantage of directly probing the sulfur environments in these chemically complex glasses, where the number of oxide components can be as large as nineteen.

Sulfur XANES have been reported for crystalline compounds containing sulfur in different coordination environments [2-5]. Sulfur can act as a cation in sulfate ( $\text{SO}_4^{2-}$ ) and sulfite ( $\text{SO}_3^{2-}$ ) environments. Sulfur can also act as an anion in sulfides, where sulfur can bond to transition metals (e.g.,  $\text{CuFeS}_2$ ), and to itself in the form of S-S doublets (e.g.,  $\text{FeS}_2$ ). Sulfur can also bond to itself and oxygen simultaneously (e.g., sodium thiosulfate:  $\text{Na}_2\text{S}_2\text{O}_3$  [3]). In consideration of this, XANES data were collected for five standards containing the sulfur environments described above, as well as for twelve borosilicate glasses having a wide range of compositions.

## EXPERIMENTAL

XANES data were collected on Beam Line 9.3.1 at the Advanced Light Source, LBNL. Average synchrotron running conditions during the data collection were 300 mA and 1.9 GeV. Fluorescence XANES data were gathered, where the Si(111) monochromator was scanned through an energy range from 2435 to 2535 eV, that included the sulfur K-absorption edge near 2470 eV for the samples of interest. Energy resolution for the beam line was about 0.3 eV. For energy calibration, XANES data were collected for  $\text{SF}_6$ , where the sulfur edge is known to be at 2486.0 eV [6]; the energy error for each spectrum is  $\pm 0.2$  eV. Sample powders were sieved so that particle sizes were 10  $\mu\text{m}$  or less for the standards and 75  $\mu\text{m}$  or less for the low sulfur concentration glasses ( $\leq 1.87$  wt.%  $\text{SO}_3$ ). For each sample, one layer of particles was deposited on kapton tape covering a 1  $\text{cm}^2$  area that was adhered to a small metal frame. The powders were mounted on a manipulator that positioned each sample into the incident X-ray beam, under vacuum at  $1 \times 10^{-7}$  torr.

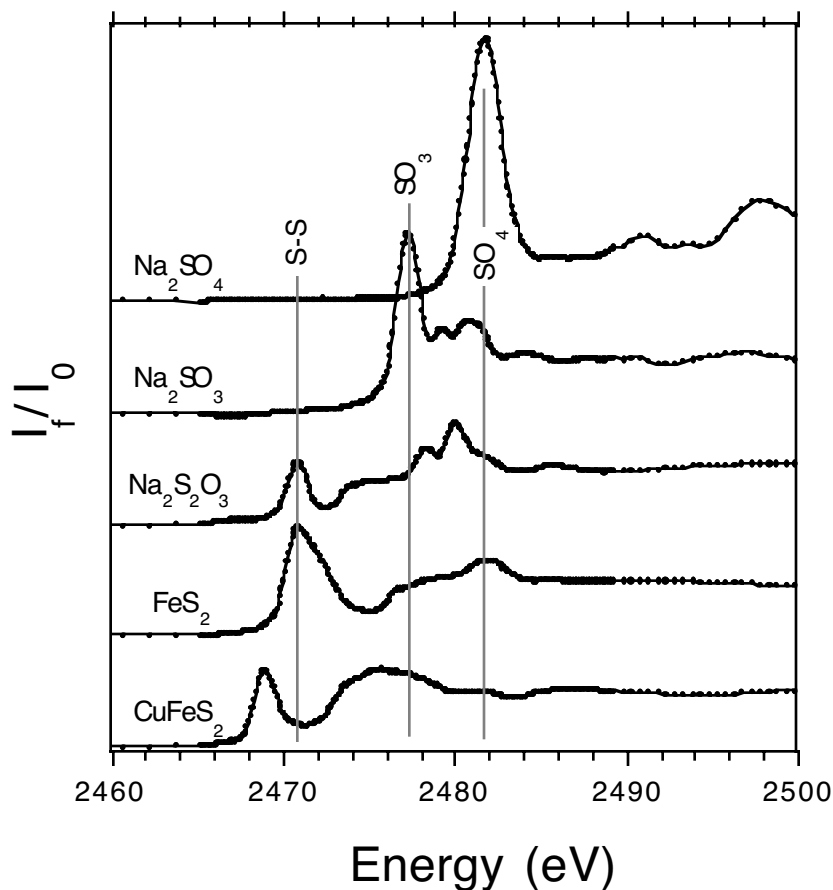


Figure 1. Normalized sulfur XANES of the standards. Edge energies for  $\text{SO}_4^{2-}$  ( $\text{S}^{+6}$ ),  $\text{SO}_3^{2-}$  ( $\text{S}^{+4}$ ), and S-S $^{2-}$  are at 2481.8, 2477.3, and 2470.8 eV, respectively; spectra are offset vertically for clarity.

## DISCUSSION

Sulfur XANES for the crystalline standards are similar to spectra presented earlier [2-5], and show a progressive shift of the sulfur K-edge to lower energies as sulfur valence decreases from  $\text{S}^{6+}$  to  $\text{S}^{2-}$  (Fig. 1). The  $\text{Na}_2\text{S}_2\text{O}_3$  spectrum is more complicated due to the two sulfur environments (S-S and  $\text{SO}_3$ ) within the  $\text{S}_2\text{O}_3$  tetrahedra.

The glasses investigated can be divided into two groups according to their XANES features. Most glasses have sulfate only, as the sulfur edges are near 2482 eV (Fig. 2 top). Four glasses have complicated sulfur edges, indicating sulfate, sulfite, and a form of S-S. (Fig. 2 bottom). The lowest energy edge feature for these four glasses is near 2472.5 eV, higher than the edge energy for S-S doublets in  $\text{FeS}_2$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (near 2470.8 eV). Sulfur K-edges near 2473 eV were measured for crystalline  $\text{Na}_2\text{S}_4\text{O}_6$  (with  $\text{S}_4$  chains), and  $\text{S}_8$  (with  $\text{S}_8$  rings)[3]. Therefore, the lowest energy edge features for these four glasses indicate S-S bonds, probably within sulfur chains containing three or more sulfurs. Further investigations are underway to determine why these two glass groups have different distributions of sulfur species and to more specifically

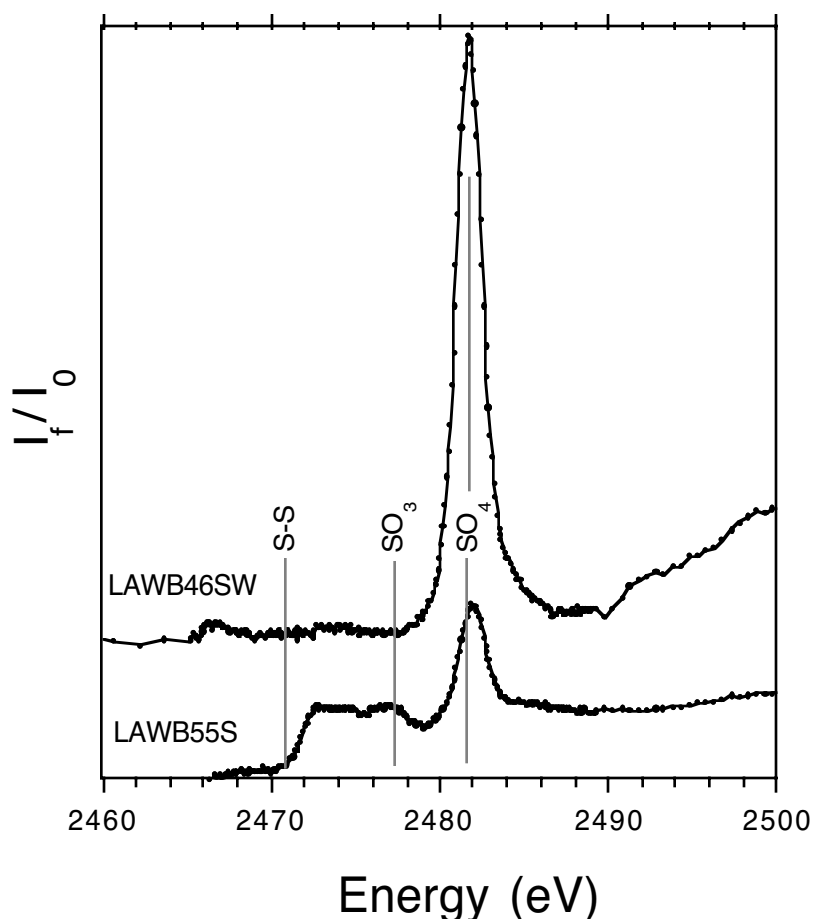


Figure 2. Normalized sulfur XANES of two representative glasses. Conventions in Figure 1 apply.

determine the nature of the S-S environments in the four glasses.

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